

Spectra Of Conjugated Molecules (SM)

Objective

The purpose of this experiment is to determine the wavelength at which vitamin A and beta-carotene adsorb light by (1) experimental measurement using a uv/vis spectrophotometer, (2) a rough estimate using the model of free electrons moving in a one dimensional box (this model is very approximate so don't expect a very close prediction), and (3) a more exact molecular modeling computation using CAChe (Scigress) software. Notice that in this experiment, you are doing activities like an experimental chemist (lab work), a theoretical chemist (derive a new relation), and a computational chemist (apply existing theory to a chemical system).

1) Experiment Instructions

See the directions that are placed with the uv/vis instrument for operating the uv/vis spectrophotometer you will be using.

We are currently using capsules as sources of vitamin A and beta-Carotene. The beta-carotene should be kept in a refrigerator in lab. Beta-carotene, because it tends to decompose with heat and light, should be kept in a refrigerator in the dark. The source should only be out long enough to get your capsule sample and then immediately return the bottle to the refrigerator.

Use a pin to puncture the beta-carotene capsule and squeeze out a tiny drop of red liquid. Stir to get it to dissolve in methanol. You should observe a colored solution.

Use a pin to puncture a vitamin A capsule and add one drop of liquid from the capsule to about 10 mL of methanol. Ignore the droplets of yellow liquid. That is oil and not the vitamin A. You want to use only the colorless liquid. Do not try to mix the yellow oil with the methanol. Wait a few minutes and pour the methanol off leaving the oil drops behind. The vitamin A will dissolve in the methanol but you cannot see it.

Structures of these molecules can be found in the *Merck Index* located in the Physical Chemistry lab or in online websites. Record the structures of these molecules in your lab notebook and in your report.

You should scan the samples from 800 to 300 nm. The uv/vis instrument uses a reference cuvet with solvent only and a sample cuvet with solute and solvent. You will use methanol as the solvent so the reference cuvet will contain only methanol. The cuvetts should be filled up to but not above the marked line and may have a specific orientation in the instrument (hold rough side so light goes through smooth side – ask instructor if not clear). Path of the light beam in a large instrument is normally parallel to the front of the instrument so if cuvet has cloudy sides and clear sides the clear sides should be on the left and right as you face instrument. In a very small uv/vis device the orientation of the beam may not be as obvious but you need to know to make sure cuvetts placed in the correct way. If all sides of cuvet are clear then there should be mark on one side of the cuvet to use as guide to place it the same each time. Cuvets should be wiped off with Kimwipe prior to placing in instrument.

In a dual beam instrument the sample and reference are run simultaneously and in a single beam instrument they are run sequentially.

The beta-carotene has certain decomposition products that may appear at lower wavelengths so for this sample we are interested in the peak that occurs at the higher wavelength. For beta-carotene you can ignore any peak that occurs below 350nm.

At the end of the experiment discard the plastic cuvetts you have used.

Place your experimental values for wavelength maximum in a table with additional columns for the calculated and CAChe computer results. One of the lab partners should include with their report the recording of absorbance versus wavelength for each conjugated molecule.

2) Particle In A Box Model And Analysis

The solution to the Schrodinger Equation that forms the theoretical basis for all chemistry can be quite complicated. However, for the special case of a particle trapped in a one-dimensional box, the solution is

$$E_n = (h^2 n^2) / (8 m L^2) \quad (1)$$

where E_n is the energy of the n th energy level, n is the integer value that specifies a specific energy level, h is the Planck's constant, m is the mass of the particle (in this case an electron), and L is the length of the box (in our case the conjugated portion of the molecule composed of alternating single and double bonds). Although it is an extremely simple approximation—so one should not expect an exact match to experiment—it is useful to consider that some of the electrons in vitamin A and in beta carotene act like they are held in a one dimensional box.

An electron goes from the highest occupied orbital (HOMO) to the lowest unoccupied orbital (LUMO) when the correct wavelength of light strikes the molecule such that the photons of this light have an energy equal to the difference between the HOMO and LUMO levels, ΔE , where

$$\Delta E = E_{n_u} - E_{n_o} = h^2 (n_u^2 - n_o^2) / (8 m L^2) \quad (2)$$

where n_u is the LUMO level and n_o is the HOMO level integer values.

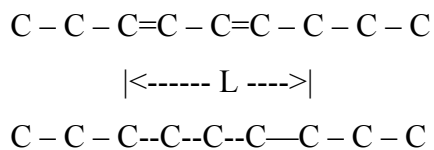
Keep in mind that n_u is always $n_o + 1$ since these are adjacent energy levels. The wavelength maximum of the uv/vis spectrum is related to the molecular structure (how many double bonds in the conjugated system). The change in energy is related to the number of double bonds, b , in the conjugated system. Prepare a table that shows how the wavelength maximum depends on the number of double bonds in a conjugated system having 3, 5, 7, 9, 11, and 13 double bonds. Include in this table the relevant parameters such as number of double bonds (b), integer value of upper level (n_u), integer value of lower level (n_o), and predicted wavelength maximum λ (nm).

Remember that this theory is very approximate and is not expected to give answers in exact agreement with experiment. Electromagnetic radiation spans about 15 orders of magnitude

(powers of ten), so if the theory agrees within 1 order of magnitude (factor of 10) or less it has made a good first approximation. Compare how the trend in the value of the predicted absorbance wavelength maximum compares to the observed absorbance wavelength maximum and how both are related to length of conjugated system – does your derived equation predict a longer conjugated system should have a greater or lesser wavelength at which absorbance occurs.

As mentioned previously, the solution to the Schrodinger equation for a particle in a one-dimensional box is given in Eq. (1) where E_n is the energy of the n th level, h is Planck constant, m is the mass of the particle, and L is the length of the box. Although it is a very simple approximation, one can assume that the electrons in a conjugated hydrocarbon behave like particles trapped in a one-dimensional box.

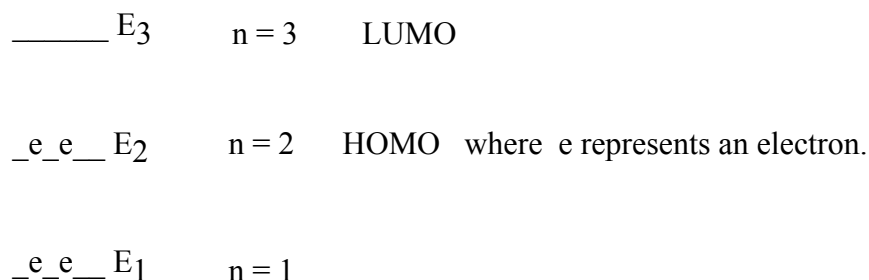
The length of the box is the length of the conjugated system (thought of as alternating single and double bonds). For example, as shown below there are two double bonds in the conjugated system ($b=2$)



However, another better model drawn above assumes the pi electrons are spread out evenly over the length L and thus each carbon-carbon bond over the conjugated system would have the same bond length. We expect this $\text{Csp}^2\text{--Csp}^2$ bond length to be the same as the bond length (l) between carbons in the conjugated benzene ring ($l = 0.139$ nm). For comparison, the C–C single bond is 0.154nm and the C=C double bond is 0.134nm. Also note that if the pi electrons that reside in a conjugated system are assumed to fill in the available energy levels two electrons per level, then a system that has b double bonds will have $2b$ delocalized electrons.

The absorption of electromagnetic radiation by the molecules can cause an electron to be excited from the highest occupied level to the lowest unoccupied level. The change in energy is thus ΔE

= $E_{n_u} - E_{n_o}$. For a molecule with two double bonds, $b=2$, an electron could be excited from the $n=2$ to $n=3$ level and the energy change would be $E_3 - E_2$. This may be represented as



This energy change can be converted to the wavelength of light if you recall that

$$\Delta E = E_{n_u} - E_{n_o} = h \nu \quad (3)$$

and

$$c = \nu \lambda \quad (4)$$

where ν is the frequency, c is the speed of light, and λ is the wavelength.

Combine the above equations to solve for λ . Use available information to estimate L and n and then calculate λ for vitamin A and beta carotene. Notice that you should relate

λ to ν and then

ν to ΔE and then

ΔE to parameters in Eq. (2) and then

n_u to n_o and then

n_u and n_o to the number of double bonds b ,

and then the length L to b and l (the bond length for sp^2 carbons in benzene $C=C$ in benzene).

Show all the steps of this derivation, number your equations, define all symbols as used, explain each step, and include proper unit conversions. Notice that in this work the goal is to obtain a generalized equation based on the particle in a box model that works for any number of double bonds in a conjugated system. You should have $\lambda =$ on the left side and each step should change the right side of the equation until you have a general solution that depends on some constants

and the number of double bonds. Combine all constants and with appropriate units to end of with a simplified but general equation. You will then use this general equation for the subsequent specific calculations. Make a table summarizing these values and results that shows how the wavelength maximum depends on the number of double bonds in a conjugated system having 3, 5, 7, 9, 11, and 13 double bonds. Also place the estimated values of λ for vitamin A and beta carotene in the table with the experimental results.

Computational Chemistry using CAChe

Background

Computational chemistry represents an exciting and rapidly developing area of modern chemistry. Molecular modeling, the major subcategory of computational chemistry, involves using a computer to predict the properties of chemical substances. For example, drug companies are using computational chemistry extensively to develop new medicinal compounds by modeling the structures of drugs and the active sites of the biological molecules where those drugs interact.

In this experiment you will use the molecular modeling software CAChe (**Computer Aided Chemistry**) to perform calculations on two substances, vitamin A and beta carotene. The Department pays about \$3,000 a year to make this powerful software available. The list of properties which CAChe can calculate is extensive, but in this experiment we will focus only on molecular structure and λ_{max} , the visible-UV wavelength of maximum absorption. Note the software in use may be changed in 2008 to Scigress. **Scigress** is a new version of CAChe with slight modifications so as you read directions if a step doesn't work exactly as written then you will need to try a logical alternative or alternatives - please record any variations on these pages and share with instructor. Please consider any trial and error as part of the fun and challenge of the experiment.

Although the computational details are largely hidden from you, this activity shows the tremendous power of computational chemistry. The computer performs an extremely large number of computations during a typical molecular-modeling calculation.

Instructions are given below that should lead you through the computation but if you need more details in how to use CAChe ([Scigress](#)), refer to the CAChe tutorial pages. Also a few pages follow the instructions below that give additional specific directions of how to carry out the calculation process.

Getting Started

If using a computer in the chemistry computer lab, move the mouse to start. The computer should already be turned on. Enter your Username and password for your OneNet Account and click OK. When you are done at the end of the lab, be sure to choose Log Off option from Shut Down, but do not turn off computer.

Create a new folder with your name. Anything you save must be placed in your folder only. **Do not save any CAChe file in any other place than in your named folder!** Expect files to be purged at the end of each semester.

Drawing Molecules

Now, double click to open the CAChe Workspace (located on the desktop screen). Enlarge the window so it fills the screen. Remember you can go to fragment library to pick up things like cyclohexane ring, benzene ring, etc. to speed up drawing molecular structures. To access fragment library you will need to go through the sequence of folders: My Computer–Disk C–Program Files–Fujitsu–CAChe–Fragment Library. **Never save anything into the fragment library!** These structures need to remain unchanged.

Use the Tutorial directions and directions below to assist you in drawing Vitamin A and Beta-carotene molecules Recall that can remove an atom using Select Tool (highlight on screen and strike delete key on keyboard). You use the Atom Tool to draw bonds between atoms. You can think of CAChe as a three-step process that includes: drawing a molecule, carrying out a

calculation, and observing the results of the calculation. If you make a mistake do not worry, you can always delete structure and start over.

Refer to tutorial for additional assistance if you need help. Follow steps below to lead you through process to draw molecules. Make sure that you select not only appropriate atom, but also correct hybridization, charge, and bond. The box with the specified charge for a neutral atom will be 0 or simply blank.

You can use Select Tool to draw a box around items or click on item to highlight. You can then remove the highlighted item by use of delete key on keyboard. You can immediately correct mistakes by choosing Undo under Edit on menu bar. The Select Tool (on Tool palette) can be used to click on a single atom or bond or to draw a box around a collection of atoms that can then be removed by striking the delete key or using the Cut or Clear choices under Edit menu.

Hold down Ctrl key and strike f key to center and size molecule. Choose Rotate from Tool palette and rotate molecule to observe from various angles. **Every time you draw a new molecule you should do Ctrl f and rotate to carefully observe the three-dimensional structure of the molecule.**

Draw a Vitamin A molecule. Under Beautify on the menu bar, choose Comprehensive to add hydrogens and adjust to standard structure. At this point you should see a proper ball and stick structure for vitamin A. Select views: Lines Only, Lines, Ball and Cylinder, and Space Filling to see how the molecule looks in different views. Rotate each view. Then return to normal ball and cylinder (or ball and stick) view. You don't need to print a copy of the molecule.

To save this molecular structure, under the File Menu select Save As. When dialog box of places to save appears, open your named folder and save there. You must save your files only in your own named folder. Please name file as Vitamin A and save. CAChe will use this file in later calculations. You can use the full name of molecules for their files but not more than 31 characters.

Under Experiment on the Menu Bar, choose New. It will ask you to save the molecule if you have not already done so. Once you have done so, an experiment window will open. Select the following choices. Property of: chemical sample, Property: optimize geometry, Using: MM3. Run this experiments and then close all open CAChe windows. You will save this optimized geometry structure.

Note: The Mechanics calculation is a classical calculation. The program considers the molecule to be a collection of spherical atoms connected by spring-like forces. The program finds the minimum energy confirmation (optimal structure) by minimizing the energy associated with the stretching, bending, and twisting forces of the forces holding the atoms together.

Repeat all the steps above necessary to draw, optimize, and save a structure for Beta-Carotene. Look carefully again at both structures (Vitamin A and Beta-Carotene) to confirm that you have the correct number of double bonds present. Now that Vitamin A and β -Carotene structures are drawn and saved, close all open windows and return to the desktop.

Project Leader

Project Leader is a spread sheet like interface that allows you to calculate a series of molecular properties on a series of molecules. We will use Project Leader to calculate a uv/vis spectra for both molecules. Project Leader often uses separate computational programs to accomplish its tasks. Open My Computer–Disk C–Program Files–Fujitsu–CAChe–PLWin. PL Win is the Project Leader software.

Mechanics estimates the optimized structure using a set of non-quantum mechanical force constants for stretching, bending, and twisting of bonds. Mechanics is very fast, but it is not as reliable as quantum calculations. The purpose of mechanics is to obtain the initial optimal structure of the molecule. Mechanics can be recognized by abbreviates such as MM2 or MM3.

MOPAC is a computer program that performs quantum mechanical calculations using appropriate approximations. While performing an extensive set of quantum mechanical calculations, MOPAC also adjusts the bond lengths and bond angles of the molecule in order to

find the most-stable, lowest-energy configuration. This process is referred to as “optimizing the geometry” or “minimizing the energy.” MOPAC is used by Project Leader to calculate a number of the properties it reports. MOPAC is a semi-empirical technique that means it has some imputed data to help speed the calculations. It is not a pure solution of the Schrodinger Equation. Semi-empirical techniques can be recognized by abbreviations such as AM1, PM3, PM5, etc. Whenever an experiment is run in CAChe a dialog windows appears that gives you choices of options and a brief explanation of the technique used. You should always read the description of the technique selected.

After you open PL Win you should observe an open table. The first column (column A) of this spreadsheet table is chemical Sample. Double click in the below the chemical sample heading (cell A-1). A dialog box will appear which will allow you to find the file for Vitamin A, in your named folder. Open this file and the name or structure should appear in the cell. Double click on the cell (cell A-2) immediately below the cell with the Vitamin A. A dialog box will appear which will allow you to find the file for Beta-Carotene, in your named folder. Open this file and the name or structure should appear in the cell.

Now double click in the top cell of column Column B next to “chemical sample”. You should get a dialog window with three boxes. Make the following selections: Left Box: Property Of–chemical sample, Middle Box: Property–lambda max uv-visible, Right Box: Using–MO-S PM3 using CI at current geometry. Read the procedure description below the boxes and note that MM2 refers to Mechanics calculation parameters and PM3 refers to MOPAC calculation parameters. Other methods would give different but hopefully similar answers. If you wish, you can try an additional different method such as the newer PM5 MOPAC calculation.

Now highlight the two cells to be evaluated 1-B and 2-B, and choose Evaluate–Cells. CAChe will proceed to perform the necessary calculations and report the answers in the cells. It may take several minutes for CAChe to do this. When values appear, Project Leader is done. Results are saved in the same folder as your editor files in the Save Here(Documents) folder. Record the results of the CAChe calculation and report them in the master table in your report.

Examine the mechanics Log, and MOPAC log files to see how energy changes as the structure is optimized.

Quit all open CAChe applications: Editor, MOPAC, ZINDO, Mechanics, Visualizer, and Project Leader, if they are still open.

The two pages that follow are merely provided to illustrate examples of determining uv/vis spectra with Scigress.

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1. Build a molecule for each of the assigned sunscreen chemicals in the Workspace/Editor.
2. Save the molecules and close the molecules in the Workspace/Editor.
3. Locate and open the program ProjectLeader on the computer. When ProjectLeader opens, a table appears on the screen with the first column labeled "chemical sample".
4. Double click in the first cell under the "chemical sample" column.
 - (Windows) An Open dialog box appears. Locate the molecule file and highlight it. Click on **Open**. The dialog box closes and the structure appears in the cell.
 - (Mac) An Open dialog box appears. Locate the molecule file and highlight it. Click on **Add**. The dialog box closes and the file name appears in the cell.
5. Repeat step 4 until you have entered all of the molecules in the chemical sample column.
6. Double click in the second column heading cell.
 - (Windows) An Enter Property dialog box opens. Click on the circle next to Property of. In the pull down menu next to it, highlight **UV/vis spectra**. Click **Next**. Highlight **excitation energy** in the Kind of property list. Click **Next**. Highlight **excitation E at MM/INDO1 geometry**.
 - (Mac) An Enter Property dialog box opens. Click on the circle next to Property of. In the pull down menu next to it, highlight **UV/vis spectra**. Click **Next**. Highlight **excitation energy** in the Kind of property list. Click **Next**. Highlight **excitation E @ MM/INDO1 geometry**.
7. Click **OK** to close the dialog box. Columns B and C say "UV/vis Spectra" and "excitation energy (cm-1)" respectively. The UV/vis spectra column contains wavelengths (nm) where there are high absorbance values. Excitation energy is the wavelength expressed in a different form (cm⁻¹).
8. Highlight the cells in the second and third columns and select **Evaluate | Cells**. It may take a while for the calculations to complete. When the calculations finish, wavelengths appear in column two and the corresponding energies in column three.
9. Save the Project in a designated location.

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General Chemistry Experiment 3 - Sunscreen and Ultraviolet Absorption

10. Open the molecule and UV spectra.

- (Windows) Return to the Workspace. Open one of the sunscreen molecules. The molecule should appear in one window, and the molecule's UV spectrum should appear in a UV-visible Transitions window. If the UV spectrum does not appear select **View | UV-visible Transitions**. *Analyze*

2. Double click on the molecule name to open one of the sunscreen molecules. A window with the molecule appears.

3. Select Analyze | Electronic Spectra. The UV spectrum opens in a new window.

11. Adjust the scale of the UV/vis graph. The range you want to look at for UVA, UVB absorption is between 270-400 nm. *300-800 nm.*

- (Windows) Double click on the x-axis or the y-axis. A View Axis Attributes dialog box appears. Change the Wavelength Range (x-axis) to go from 250 to 400 nm. Adjust the Intensity Range (y-axis) to best represent the data. Click **OK**.

4. Double click on the x-axis. The View Parameters box appears. Set the range to 250 in the "Left" box and 400 in the "Right" box. Set

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Beer's Law
Beer-Lambert Law

Spectra are often characterized by the *transmittance* T at a given wavelength; this is defined by

$$T \equiv \frac{I}{I_0}$$

where I is the intensity of light transmitted by the sample and I_0 is the intensity of light incident on the sample. When the sample is in solution and a cell must be used, I is taken to be the intensity of light transmitted by the cell when it contains solution while I_0 is taken to be the intensity of light transmitted by the cell filled with pure solvent. Another way of describing spectra is in terms of the *absorbance* A , where

$$A \equiv \log \frac{I_0}{I}$$

A completely transparent sample would have $T = 1$ or $A = 0$, while a completely opaque sample would have $T = 0$ or $A = \infty$.

The absorbance A is related to the path length d of the sample and the concentration c of absorbing molecules by the Beer-Lambert law,⁵

$$A = \epsilon cd$$

where ϵ is called the *molar absorption coefficient* when the concentration is expressed in moles per unit volume.† The quantity ϵ is an intrinsic property of the absorbing material that varies with wavelength in a characteristic manner; its value depends only slightly on the solvent used or on the temperature. The SI unit for ϵ is $\text{mol}^{-1} \text{m}^2$, but a more practical and commonly used unit is $\text{mol}^{-1} \text{L cm}^{-1}$, which corresponds to using the concentration c in mol L^{-1} and the path length d in cm.

For quantitative measurements it is important to calibrate the cells so that a correction can be made for any small difference in path length between the solution cell and the solvent cell. For analytical applications, one must check the validity of Beer's law, since slight deviations are often observed and a calibration curve of absorbance versus concentration is then required. Such quantitative techniques are described elsewhere⁵ and will not be necessary in the present work.